Sodium hypochlorite, in the concentrations recommended by Birch and Norris (*1*), can also be used for an oxidizing agent. Accordingly, 20 cc. of sodium hypochlorite were added to 20 cc. of the naphtha solution in a separatory funnel and shaken for 15 minutes. The naphtha was washed 3 times with water and then analyzed for its sulfur content. The removal of the pentamethylene sulfide from the three naphthas was practically complete.

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Note on the Methanol Equilibrium[1]

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Equilibrium Constants of Various Investigators

SEVERAL papers dealing with the calculation of the free-energy change for the methanol synthesis reaction have recently appeared. Kelley (*7*) published the first calculation, utilizing the free energy of formation of liquid methanol at 298° K. as determined by Parks (*11*) from thermal data, combined with the other necessary thermal data to obtain ΔF for the reaction as a function of temperature. Smith (*12*) and also Francis (*5*) repeated the calculation using somewhat different data, but obtaining essentially the same result. More recently Kelley (*8*) has recalculated ΔF for this reaction, using his own determination of the entropy of methanol (*9*) and other more recent thermal data.

All the calculated ΔF's lead to values of $K_p \left(\frac{P_{CHO_3H}}{P_{CO} \times P^2_{H_2}}\right)$ which do not agree at all with the published experimental results on the high-pressure synthesis of methanol (*4*). Part of this difference, but certainly not all of it, may be due to deviations from the ideal gas laws at the high pressures employed in the synthesis. On the other hand, Smith and Branting (*13*) have made a careful direct determination of the equilibrium constant at atmospheric pressure, thus eliminating any question of the effect of pressure on the constant.

Two earlier indirect experimental determinations of the methanol equilibrium had been made. Ghosh and Chakravarty (*6*) attempted to measure the equilibrium constant at atmospheric pressure for the two reactions

$$CH_3OH = HCOH + H_2$$
$$HCOH = CO + H_2$$

Combining the two equations for K_p as a function of temperature, one can obtain K_p for methanol synthesis as a function of T. Their work appears to be rather doubtful and the constant is not even of the same order of magnitude as the other experimentally determined ones. Christiansen (*3*) determined the equilibrium constants for the two reactions

$$CH_3OOCH + 2H_2 = 2CH_3OH$$
$$CH_3OH + CO = CH_3OOCH$$

at atmospheric pressure and temperatures around 200° C. He gives an equation for K_p of the methanol reaction as a function of temperature.

There still remains a considerable discrepancy between the calculated and observed results, as shown by Table I.

Note—Since this paper was written, the paper by Newitt, Byrne, and Strong [*Proc. Roy. Soc. (London)*, **A123**, 236 (1929)] appeared. They determined the equilibrium constant for the reaction at pressures around 100 atmospheres, approaching equilibrium from both sides. They express their results by the equation

$$\Delta F = 70.5\ T - 30{,}500$$

from which the following results for comparison with those in Table I have been calculated:

T (° K.)	ΔF	K_p
298.1	− 9,484	9.01×10^6
600	+ 11,800	5.03×10^{-5}
673	+ 16,950	3.13×10^{-6}

It is best to use the value at 600° K. for comparison as that is within their experimental range. Their result is not in agreement with either Kelley's calculated K_p or Smith and Branting's experimental one. The difference from the latter cannot be explained on the basis of the pressures because the deviation is in the wrong direction.

It is true that some authors (*1*, *2*, *10*) have attempted to calculate K_p for the methanol reaction from the Nernst approximation formula and apparently a fair agreement has been obtained with the observed results on the high-pressure synthesis. However, in view of the very unsound theoretical foundation for this formula and its complete failure in many well-established equilibria, we must regard this agreement as wholly fortuitous.

Reason for Discrepancy between Observed and Calculated Constants

The purpose of the present note is to indicate a possible explanation for this discrepancy between the calculated and observed equilibrium constants, and also to show more clearly than has been done before what data are used for the calculation, the relative importance of the various sets of data, and to point out a serious difficulty with all calculations of this type. In the discussion the following equations will be referred to:

$CO + 2H_2 = CH_3OH$ (gas, 1 atm.)	(1)
CH_3OH (gas, 1 atm.) = CH_3OH (gas, 0.162 atm.)	(2)
CH_3OH (liquid) = CH_3OH (gas, 0.162 atm.)	(3)
$C + {}^1/_2O_2 + 2H_2 = CH_3OH$ (liquid)	(4)
$CO + 2H_2 = CH_3OH$ (liquid)	(5)
CH_3OH (liquid) $+ 1^1/_2O_2 = CO_2 + 2H_2O$ (liquid)	(6)
$H_2 + {}^1/_2O_2 = H_2O$ (liquid)	(7)
$CO + {}^1/_2O_2 = CO_2$	(8)
$C + O_2 = CO_2$	(9)
$CO_2 + H_2 = CO + H_2O$	(10)
$C + CO_2 = 2CO$	(11)
$C + {}^1/_2O_2 = CO$	(12)

The heat-content and free-energy changes for these reactions will be indicated by the usual symbols with subscripts to show to which equation they refer. In addition, the following symbols will be used:

S_M = entropy of liquid methanol
S_C, S_H, and S_O = entropies of carbon, hydrogen, and oxygen, respectively
S_M = entropy of gaseous methanol at 1 atmosphere
S_{CO} = entropy of carbon monoxide

Unless otherwise indicated, all gases are considered to be

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Table I—Values of ΔF and of K_p Calculated from Equations Given by Various Authors

Author	$\Delta F_{298.1}$	K_p at 298.1° K.	ΔF_{600}	K_p at 600° K.	ΔF_{673}	K_p at 673° K. (400° C.)
Kelley (7)	−10950	1.05×10^{8}	+3900	3.80×10^{-2}	+ 7650	3.28×10^{-3}
Smith (12)	−10850	8.90×10^{7}	4220	2.90×10^{-2}	7958	2.61×10^{-3}
Francis (5)	−11500	2.63×10^{8}	3570	5.01×10^{-2}	7218	4.53×10^{-3}
Kelley (8)	−9640	1.15×10^{7}	6920	3.03×10^{-3}	11026	2.63×10^{-4}
Smith and Branting (13)	−7980	7.08×10^{5}	9990	2.32×10^{-4}	14433	2.05×10^{-5}
Christiansen (3)	.....	1.66×10^{6}	..	2.24×10^{-4}	...	2.28×10^{-5}
Brown and Galloway, assuming ideal gases (2)						1.98×10^{-5}

at 1 atmosphere. In the treatment immediately following all thermal quantities will be referred to 298.1° K.

ΔF_1 may be calculated in different ways by suitable combinations of these equations. One method is that used by Kelley and others, and may be outlined as follows:

$$\Delta F_5 = \Delta F_4 - \Delta F_{12} \quad (13)$$
$$\Delta F_4 = \Delta H_4 - T\Delta S_4 \quad (14)$$
$$\Delta H_4 = \Delta H_9 + 2\Delta H_7 - \Delta H_6 \quad (15)$$
$$\Delta S_4 = S_M - S_C - {}^1/_2 S_O - 2S_H \quad (16)$$
$$\Delta F_4 \text{ (free energy of formation of liquid methanol)} = \Delta H_9 + 2\Delta H_7 - \Delta H_6 - T(S_M - S_C - {}^1/_2 S_O - 2S_H) \quad (17)$$

ΔF_{12} is obtained by combination of Reactions 11 and 8 or 7, 10, and 11. According to Lewis and Randall the two methods agree well, so we will choose the first:

$$\Delta F_{12} = \Delta F_8 + \Delta F_{11} \quad (18)$$

ΔF_1, the desired free-energy change, is equal to

$$\Delta F_5 + \Delta F_3 - \Delta F_2 \quad (19)$$

Finally,

$$\Delta F_1 = \Delta H_9 + 2\Delta H_7 - \Delta H_6 - T(S_M - S_C - {}^1/_2 S_O - 2S_H) - \Delta F_8 - \Delta F_{11} + \Delta F_3 - \Delta F_2 \quad (20)$$

$\Delta F_3 = 0$, and ΔF_2 is readily calculated from the simple thermodynamic relation $\Delta F = R\,T \ln (P_2)/(P_1)$, assuming ideal gases. All the other quantities are the result of experimental measurement, although it is recognized that the actual measurements were often made at entirely different temperatures and the quantity used was obtained through extrapolation or interpolation using well-known thermodynamic relations and specific heat data. The following values of the various quantities have been selected and their source indicated:

$\Delta H_9 = -94{,}270$	Roth and Naeser, *Z. Elektrochem.*, **31**, 461 (1925). Based on beta-graphite
$\Delta H_7 = -68{,}320$	International Critical Tables (calcd. to 25° C.)
$\Delta H_6 = -170{,}650$	Richards and Davis, *J. Am. Chem. Soc.*, **42**, 1599 (1920) (cor. to 25° C. and to 15° calories)
$\Delta F_2 = -1070$	Calculated from $RT \ln \frac{P_2}{P_1}$
$\Delta F_8 = -61{,}750$	Lewis and Randall textbook
$\Delta F_{11} = 29{,}110$	Eastman, Bur. Mines, *Inf. Circ.* **6125**
$S_M = 30.3$	Kelley (9)
$S_C = 1.3$	Lewis and Randall
$S_O = 48.9$	Kelley (9)
$S_H = 31.25$	Kelley (9)

Substituting these values in Equation 20, we have

$$\Delta F_1 = -94{,}270 - 136{,}640 + 170{,}650 - 298.1\,(30.3 - 1.3 - 24.5 - 62.5) + 61{,}750 - 29{,}110 + 1070 = -9250$$

A simpler method of getting ΔF_1 is the following:

$$\Delta F_1 = \Delta H_1 - T\Delta S_1$$
$$\Delta H_1 = 2\Delta H_7 + \Delta H_8 - \Delta H_6 + \Delta H_3 - \Delta H_2$$
$$\Delta S_1 = S_m - S_{CO} - 2 \times S_H$$
$$S_m = S_M + \frac{\text{latent heat of vaporization at 0.162 atm.}}{298} + R \ln \frac{0.162}{1}$$

The latent heat at 0.162 atmosphere is calculated from the Clausius–Clapeyron equation to be 9100 calories.

$$S_m = 30.3 + \frac{9100}{298} - 1.987 \times 2.303 \times 0.791 = 57.2$$

S_{CO} (Lewis and Randall) = 45.6

Finally, $\Delta F_1 = -136{,}640 - 68{,}100 + 170{,}650 + 9100 - 298\,(57.2 - 45.6 - 62.5) = -9810$

This second method is interesting in that it involves no equilibrium measurements whatever, but only heats of combustion, a heat of vaporization, and three entropies.

It is seen clearly from these calculations that the quantity sought is the result of a difference of several very much larger quantities, and it takes only a small percentage error in some of the large ΔH's to make a considerable difference in the calculated ΔF. A given percentage error in the absolute entropies is not nearly so important as the same error in one of the ΔH's. Thus, using Parks's old value for S_M of 32.6, one gets −9950 for ΔF by the first method given above. Now Richards and Davis state that their heat of combustion of methanol was the least satisfactory of any of the heats of combustion given by them, and that there were evidences of incomplete combustion. If this quantity were assumed to be only 0.75 per cent low, ΔF_1 would then become −7970, in very close agreement with the result given by Smith and Branting's equation.

Note—It may be noted in passing that Thomsen's value for the heat of combustion of gaseous methanol at 18° C. and constant pressure is 182,230 calories. Allowing 9200 calories for the heat of vaporization at 18° C. gives 173,030 for heat of combustion of liquid methanol, a value which would throw K_p about as far off on the other side of Smith and Branting's figure.

In other words, a calculation of the free-energy change for the methanol-synthesis reaction, though based on the third law, and therefore requiring a knowledge of absolute entropies is nevertheless far more dependent on exact data for the various heats of reaction than on the entropy data. This is a point frequently overlooked by many who attempt to argue about the validity of the third law on the basis of such calculations. From a practical standpoint it means that, if we are to calculate, even roughly, equilibria for reactions of this type, we must have very accurate heat-of-reaction data. As a further concrete illustration of this fact it may be readily calculated that, if the value for the heat of combustion of methanol were in error by only 0.10 per cent, the K_p for the reaction at 298.1° K. would be in error by approximately 33 per cent as a result.

Whereas there may be other explanations of the discrepancy between calculated and directly measured values of K_p for the methanol synthesis reaction, the above simple explanation seems to be entirely adequate to account for it and, at the same time, attention has been called to an important fact bearing on the calculation of similar equilibria.

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